Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

ELECTRICAL CONDUCTIVITY IN THE FUSED SALT SYSTEM $PbCl_2$-LiCl

S.A. Mikhail and C.R.K. MacLean
Physical Chemistry Section
Extractive Metallurgy Laboratory

May 1984

This document is an unedited manuscript prepared primarily for circulation and discussion within the Department. It does not represent final opinion of the Canada Centre for Mineral and Energy Technology (CANMET)

Ce document est un manuscrit provisoire non-révisé préparé principalement pour fin de discussion et de commentaire au sein du Ministère. Il ne représente pas l'opinion définitive du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

Project MRP-3.4.0.2.02
Hydrometallurgical Lead Process

11 pp

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT MRP/MSL 84-60 (IR)

JUL 20 1984

MICROMEDIA

ELECTRICAL CONDUCTIVITY IN THE FUSED SALT SYSTEM $PbCl_2$-LiCl

by

S.A. Mikhail* and C.R.K. MacLean**

ABSTRACT

Specific conductivities in the molten salt system $PbCl_2$-LiCl were measured between 417 and 563°C using a silica glass capillary cell with an ac conductivity bridge. Conductivity increased linearly with temperature and also with increasing LiCl content in the melt. The temperature coefficient of the conductivity showed little variation with composition. The data gave no indication of complex ion formation in the melt.

---

*Research Scientist and **Technologist, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth St., Ottawa, Ontario K1A 0G1.

CONDUCTIVITE ELECTRIQUE DANS LE SYSTEME DES SELS FONDUS $PbCl_2$-LiCl

par

S.A. Mikhail* et C.R.K. MacLean**

RESUME

La conductivité spécifique dans le système des sels fondus $PbCl_2$-LiCl a été mesurée entre 417 et 563°C dans une cellule capillaire en verre de silice au moyen d'un pont de conductivité c.a. La conductivité a augmenté linéairement avec la température et les isothermes de conductivité ont révélé que cette dernière augmente avec la teneur du sel en LiCl. Le coefficient de température de la conductivit. a peu varié en fonction de la composition. Les données ne laissent croire à aucune formation d'ions complexes dans le sel fondu.

---

*Chercheur scientifique et **Technologue, Laboratoires des sciences minérales, CANMET, Energie, Mines et Ressources Canada, 555, rue Booth, Ottawa (Ontario), K1A 0G1.

INTRODUCTION

In response to increasing environmental concerns and requirements for in-plant hygiene many workers are actively searching for alternative methods for the production of lead metal from sulphide concentrates to replace the conventional sintering and blast furnace technology. A project to study the viability of extracting lead from lead concentrates using hydrometallurgical methods has been initiated at the Canada Centre for Mineral and Energy Technology (CANMET). In this project, the concentrate is leached with hot ferric chloride and brine solution to produce lead chloride, which is then treated by electrolysis in an aqueous solution or molten salt bath to produce metallic lead. One part of this project is concerned with the treatment of lead chloride by molten salt electrolysis.

Due to its high vapour pressure, its relatively high melting point and some solubility for molten lead, $PbCl_2$, on its own, is unsuitable for electrolysis. Previous work at the U.S. Bureau of Mines (1-3) indicated that molten mixtures of LiCl-KCl or NaCl-KCl may be used as solvents for $PbCl_2$ in the electrolysis process. In the first part of this work, conductivity measurements were reported in the ternary systems $PbCl_2$-LiCl-KCl and $PbCl_2$-NaCl-KCl (4,5). Conductivities and other physical properties of the binary systems $PbCl_2$-KCl, LiCl-KCl, $PbCl_2$-NaCl and NaCl-KCl were reviewed by Janz et al. (6,7). The phase diagram of the system $PbCl_2$-LiCl was determined by Gromakov and Gromkova (8) and density and surface tension studies were reviewed by Janz et al. (6). The only data available on electrical conductivities in the system $PbCl_2$-LiCl were determined between 600 and 700°C and were presented only in graphical form (9). In the present investigation determinations were made at lower temperatures, in the range of interest for lead recovery by electrolysis in the ternary system $PbCl_2$-LiCl-KCl. The conductivities of the individual salts, $PbCl_2$ and LiCl, were determined by several investigators and a review and assessment of their results was given by Janz et al. (10).

MATERIALS AND EXPERIMENTAL PROCEDURE

The starting materials were "Baker Analysed" reagent grade $PbCl_2$ (99.9%) and anhydrous LiCl, 99.8% purity and less than 0.25 mm particle

size, from CERAC Inc., Wisconsin, U.S.A. The identity of the two compounds was verified by X-ray diffraction. Semi-quantitative spectrochemical analysis indicated the following major impurities in $PbCl_2$: Al (0.01%), Fe (0.001%), Si (0.001%), Cu (0.007%), Ag (0.0009%) and Mg (0.0003%) and in LiCl: K (0.01-0.1%), Si (0.005%), Na (0.005%), Cu (0.001%), Al (0.001%) and Mg (0.001%). The lead chloride was dried at 150°C under vacuum for several hours and stored in a dry box. The LiCl was subjected to the HCl-Ar-vacuum treatment described previously (4). The handling of the starting materials was always done in a dry box.

The equipment and procedure employed for the conductivity measurements have been described in detail (4). The cell constant (in the order of 550-750 cm^{-1}) was determined by measuring the electrical conductance of a KCl solution of a known concentration at 25°C (11). The cell constant was also checked before and after each series of experiments and a maximum change of 0.5% was detected. Conductivity measurements were made using 1 and 3 kHz frequencies available with the ac conductivity bridge; the difference in the measured values did not exceed 0.1%.

RESULTS AND DISCUSSION

The specific conductivity κ (siemens cm^{-1}) was determined from the electrical conductance using the relationship:

$$\kappa = k.K_{cell} \qquad (1)$$

where k is the measured electrical conductance (S) and K_{cell} is the cell constant (cm^{-1}).

The specific conductivity of pure lead chloride was determined between 497 and 523°C and the results were found to be approximately 1 to 2% higher than those obtained by Lantratov and Mbiseeva (12) for the same temperature range. The results of the conductivity measurements are presented in Table 1 as the least squares fit of the specific conductivity versus temperature (in Kelvin) according to the following equation:

$$\kappa = a + bT \qquad (2)$$

where a and b are constants. The total experimental uncertainty in the cell constant, temperature and salt composition was estimated to be 2%. Extrapolations to the temperature range 600 to 700°C, using Equation 2 with the data in Table 1, gave results which were in fair agreement with those given by Klemm and Monse (9), considering the possible errors due to extrapolation and the uncertainties in estimating values that were presented in graphical form only. The mean difference between 24 extrapolated specific conductivity values and the values read from the graphs given by Klemm and Monse was less than 2%, and the maximum difference was about 9%.

Table 1. Least squares fit of the electrical conductivity (κ/S.cm^{-1}) vs temperature (T/K) for various compositions in the system $PbCl_2$-LiCl

Mol % $PbCl_2$	Temp. Range °C	$\kappa = a + bT$		Standard Error of Estimate	Correlation Coefficient
		-a	b x 10^3		
100	497-523	2.5512	5.211	±0.0010	0.9999
90	482-540	2.6535	5.445	0.0025	0.9998
80	460-530	2.6519	5.596	0.0033	0.9997
75	448-530	2.6829	5.733	0.0045	0.9997
70	437-530	2.6763	5.818	0.0038	0.9998
64.1	417-530	2.6006	5.834	0.0072	0.9996
60	440-530	2.5142	5.815	0.0035	0.9998
55	447-542	2.4005	5.778	0.0083	0.9991
50	470-549	2.1312	5.652	0.0032	0.9998
45	485-542	1.9484	5.596	0.0042	0.9995
40	504-534	1.8764	5.700	0.0038	0.9991
35	520-550	1.3100	5.223	0.0013	0.9999
30	541-563	1.6223	5.821	0.0026	0.9996
25*	548	κ = 3.41 S.cm^{-1}			

*Measurement at 548°C only.

The temperature range over which the conductivity of each melt was measured was limited by the liquidus temperature in the $PbCl_2$-LiCl system and by volatilization. During the experiments, the volatilization of $PbCl_2$ was noticeable when the temperature exceeded 500°C. Figure 1 shows the corelation between specific conductivity and temperature for various $PbCl_2$-LiCl solutions. It is apparent that the influence of $PbCl_2$ concentration on the conductivity is more pronounced at the LiCl-rich side of the system. The temperature coefficient of the conductivity, b, was found to

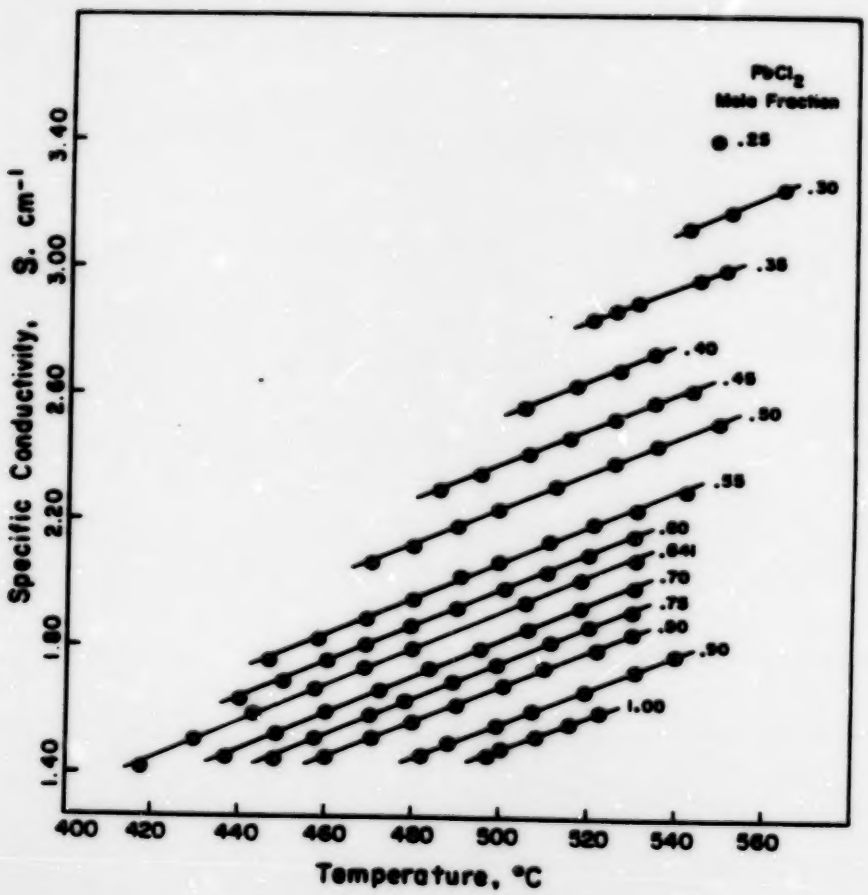

Figure 1: Temperature dependence of the specific conductivity in the system $PbCl_2$-LiCl.

be fairly insensitive to changes in composition and to lie within the range 5.2×10^{-3} to 5.9×10^{-3} $S.cm^{-1}.deg^{-1}$ for all compositions investigated.

The results are also presented in Figure 2 as specific conductivity isotherms together with the liquidus curve of the system $PbCl_2$-LiCl as determined by Gromakov and Gromakova (8). The conductivity increase observed with increasing LiCl content in the melt is consistent with the higher specific conductivity of LiCl, 5.92 $S.cm^{-1}$ at 650°C (7), compared to $PbCl_2$, 2.14 $S.cm^{-1}$ at 650°C (6). Molar and equivalent conductivities were not calculated due to the lack of density data in the system $PbCl_2$-LiCl at tempertures below 600°C for the range of compositions under investigation. The absence of minima in the specific conductivity isotherms, however, suggests that the equivalent conductivity isotherms would not show minima either, and it may be inferred that the formation of complex ions of the type $PbCl_3^-$ or $PbCl_4^{2-}$ is not significantly affecting the electrical conductivity in this system, in contrast to some other lead chloride - alkali chloride systems. Minima occur in equivalent conductivity isotherms for lead chloride - alkali chloride systems with large monovalent cations, i.e., for $PbCl_2$-KCl (12,13), $PbCl_2$-RbCl (14) and $PbCl_2$-CsCl (14); the effect becomes more marked as the monovalent cations radius increases from K^+ (r=0.133 nm) to Rb^+ (r=0.147 nm) to Cs^+ (r=0.167 nm). In the $PbCl_2$-NaCl system, with the smaller Na^+ ion (r=0.097), there is no minimum in the equivalent conductivity isotherm (14). Such lead-chloride complexes apparently are not stable in the presence of the smaller more polarizing cations (14); the results of the present investigation are consistent with this conclusion. The absence of significant complexing in $PbCl_2$-LiCl melts has been indicated also by X-ray diffraction studies (15).

ACKNOWLEDGEMENTS

The authors wish to thank W.S. Bowman for the least squares computer fitting of the equations to the experimental data and D.P. Palombo for the spectrographic analysis.

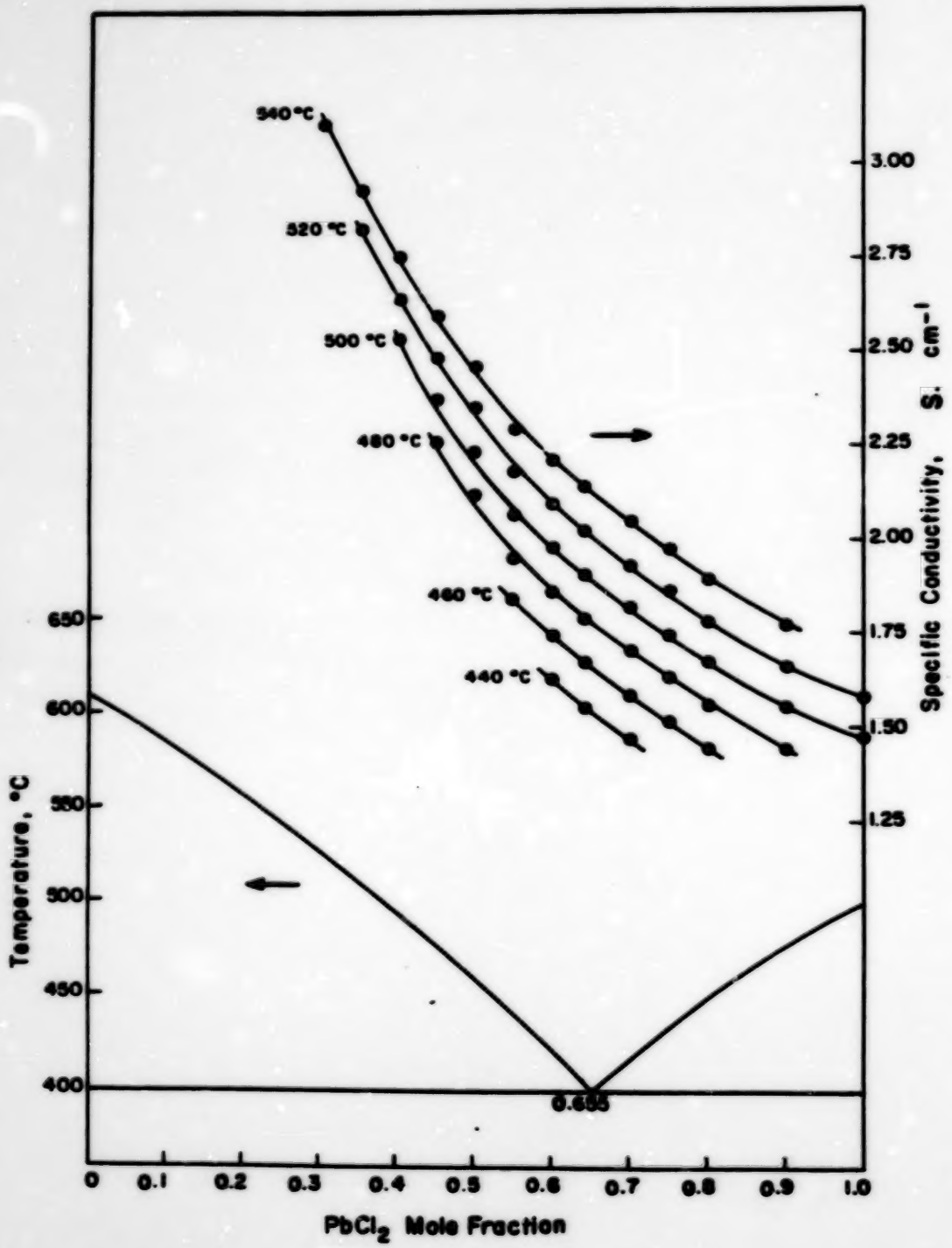

Figure 2: The phase diagram (8) and specific conductivity isotherms for the system $PbCl_2$-LiCl.

REFERENCES

1. Murphy, J.E., Haver, F.P. and Wong, M.M. "Recovery of lead from galena by a leach electrolysis procedure"; Report of Investigations 7913; U.S. Bureau of Mines; 1974.
2. Haver, F.P., Elges, C.H., Bixby, D.L. and Wong, M.M. "Recovery of lead from lead chloride by fused salt electrolysis"; Report of Investigations 8166; U.S. Bureau of Mines; 1976.
3. Wong, M.M. and Haver, F.P. "Fused-salt electrolysis for production of lead and zinc metals"; in "Molten Salt Electrolysis in Metal Production"; edited by D. Temple; Inst of Min and Metall, London; 21-29; 1977.
4. Mikhail, S.A., MacLean, C.R.K. and Webster, A.H. "Electrical conductivity in the fused salt system $PbCl_2$-LiCl-KCl"; Division Report MRP/MSL 84-42 (IR); CANMET, Energy, Mines and Resources Canada; 1984.
5. Mikhail, S.A., MacLean, C.R.K. and Webster, A.H. "Electrical conductivity in the fused salt system $PbCl_2$-NaCl-KCl"; Division Report MRP/MSL 84-48 (IR); CANMET, Energy, Mines and Resources Canada; 1984.
6. Janz, G.J., Tomkins, R.P.T., Allen, C.B., Downey, J.R. Jr., Gardner, G.L., Krebs, U. and Singer, S.K. "Molten salts: Chlorides and mixtures. Electrical conductance, density, viscosity and surface tension data"; J Phys Chem Ref Data 4:871-1178; 1975.
7. Janz, G.J., Allen, C.B., Bansal, N.P., Murphy, R.M. and Tomkins, R.P.T. "Physical properties data compilations relevant to energy storage. II. Molten salts: Data on single and multi-component salt systems"; National Standard Reference Data System - National Bureau of Standards, NSRDS-NBS 61, Part 2; Washington, U.S. Dept. of Commerce; 1979.
8. Gromkov, S.D. and Gromkova, L.M. "The liquidus curve (mathematical) application in binary systems"; Zhur Fiz Khim 29:745-749; 1955.
9. Klemm, A. and Monse, E.U. "Transport measurements for the determination of mobilities of ^6Li, ^7Li and Pb in the molten salt system LiCl-$PbCl_2$"; Z Naturforschg 12:319-334; 1957.

10. Janz, G.J., Dampier, F.W., Lakshminarayanan, G.R., Lorenz, P.K. and Tomkins, R.P.T. "Molten salts: Volume 1, Electrical conductance, density and viscosity data"; National Standard Reference Data System - National Bureau of Standards, NSRDS-NBS 15; Washington, U.S. Dept. of Commerce; 1968.

11. Jones, G. and Bradshaw, B.C. "The measurement of the conductance of electrolytes . V. A redetermination of the conductance of standard potassium chloride solutions in absolute units"; J Am Chem Soc 55: 1780-1800; 1933.

12. Lantratov, M.F. and Moiseeva, O.F. "The electrical conductivity of molten-salt mixtures. I. The $PbCl_2$-KCl system"; Russ J Phys Chem 34: 171-175; 1960.

13. Bloom, H. and Heymann, E. "The electrical conductivity and the activation energy of ionic migration of molten salts and their mixtures"; Proc Royal Soc A 188:392-414; 1947.

14. Bloom, H. and Macky, C.J. "The electrical conductance of the molten salt systems $PbCl_2$+NaCl, $PbCl_2$+RbCl, and $PbCl_2$+CsCl"; Aust J Chem 23: 1523-1530; 1970.

15. Ohno, H., Yoroki, M. and Furukawa, K. "Structural analysis of some molten materials by X-ray diffraction. Part 5. LiCl, $PbCl_2$ and their mixtures"; J Chem Soc Faraday Trans I 74:1861-1870;1978.